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EDITORIAL NOTE

Studies in Hevea Rubber

The investigations recorded in a series of papers published under the above general title have been undertaken at the Rubber Research Institute of Malaya by Dr. G. F. Bloomfield, of the British Rubber Producers' Research Association.

The work forms part of a joint programme of fundamental research undertaken by the British Rubber Producers' Research Association, and the Rubber Research Institute of Malaya.

Dr. Bloomfield came to Malaya in September 1948, and worked in the R.R.I. laboratories in Kuala Lumpur until January 1951. During the latter part of his stay, permanent members of the Institute's staff co-operated with him in the development of new lines of work arising from his fundamental studies.

The full series consists of six papers; Parts III and IV are contained in the present Communication.

Editor.

STUDIES IN HEVEA RUBBER

Part III

Fractionation of Fresh Rubber and the Interpretation of Viscometric and Osmotic Data

By

George F. Bloomfield and Graham W. Drake

Fractionation of the rubber hydrocarbon in fresh Hevea latex reveals a wide molecular weight distribution between the limits 50,000 to several millions, with the major proportion of the hydrocarbon in the high molecular range of a million and over. Osmotic data have been used to show that the relationship between intrinsic viscosity and molecular weight is more correctly represented by an equation of type $[\eta] = KM^{\alpha}$ than by the linear relationship $[\eta] = KM$. The presence of gel is a complicating factor in the interpretation of viscosity data. There is a considerable body of evidence indicating changes in the molecular symmetry of rubber in changing from good to poor solvents and in varying the temperature of solutions of rubber in poor solvents; these effects are more marked with the larger molecules than with the smaller ones.

When one is dealing with a sensitive polymer such as the hydrocarbon of purified Hevea rubber, fractionation by precipitation[1-6] has an outstanding advantage over that involving diffusion into mixed solvents[2, 7], because it can be completed in a much shorter period. For this reason, fractionation by precipitation has been used exclusively in the present series of investigations.

Table I shows the results of fractionation of an unpurified rubber, a solution of which was obtained at the tree by allowing the latex to drip into benzene, shaking to dissolve the rubber, and removing the water by reduced pressure azeotropic distillation (see Part I). Sufficient of a benzene and methanol (30/70 by volume) mixture was added to give incipient precipitation at 35°, and the precipitate was dissolved by warming to 40°. The solution was progressively cooled until sufficient precipitate had accumulated (as judged visually), after which the supernatant liquid was siphoned off under nitrogen pressure into a nitrogen-filled flask. A series of fractions was then similarly obtained by successively cooling to progressively lower temperatures. Only solvents freshly distilled under nitrogen were used in the present

series of investigations, and these were saturated with nitrogen before use*. No antioxidant was introduced other than that already present in the rubber.

Table I

Benzene-methanol fractionation of a dehydrated solution of latex from Tree 17.

Pptn. temp. of fraction	% of rubber in fraction	Intrinsic viscosity
38.3°	17.5	Insoluble
36.2°	26	5.78 in benzene + 15% methanol
29.0°	47.5	9.94 in benzene
Residual solution ..	9	3.34 in benzene

(A solution of the 36.2° fraction, redissolved in benzene, contained a little gel).

In Table II are to be found fractionation data after preliminary removal of benzene-insoluble gel from one-year old smoked sheet prepared from the trees 14, 15 and 17 studied previously (see Part I). The rubbers were given a preliminary extraction with acetone (under nitrogen) at 30°, dried in high vacuum and were then covered with benzene (100 ml. per g.) for 3 days at 30°, the flasks being inverted twice daily. The sol phase was decanted, 70/30 methanol-benzene was added to produce turbidity at 30° and the solution was progressively cooled. Also included in Table II is a rather more refined fractionation of the vacuum-dried fresh coagulum from tree 14. The apparent high gel content arose from experimental difficulty in extracting efficiently the very weak and enormously swollen gel phase; inversion of the flask was impracticable through risk of dispersion. From the data presented in Part II of this series it is certain that the gel-content quoted is too high, but the fractionation data for the sol phase are nevertheless valid.

* In order to avoid repetition of detail it can be assumed that, unless specified to the contrary, all experimental work was conducted in an atmosphere of nitrogen using nitrogen-saturated solvents.

Table II

Fractionations after removal of benzene-insoluble gel.

Rubber	Component	% in rubber	Intrinsic viscosity	N%
Smoked sheet tree 14 ..	Whole rubber* ..	100	5.65	—
	Gel ..	31	—	0.94
	Fraction pptd. at 29.3° ..	15	11.45	0.22
	Fraction in solution ..	54	5.43	0.06
Smoked sheet tree 15 ..	Whole rubber* ..	100	Part insol.	—
	Gel ..	37	—	1.17
	Fraction pptd. at 29.3° ..	22	10.31	0.14
	Fraction in solution ..	41	5.45	0.03
Smoked sheet tree 17 ..	Whole rubber* ..	100	7.28	—
	Gel ..	37	—	0.94
	Fraction pptd. at 29.3° ..	24	10.75	0.19
	Fraction in solution ..	39	6.67	0.14
Vacuum-dried coagulum tree 14	Whole rubber ..	100	5.46	
	Gel ..	63.7	—	0.51
	Fraction pptd. at 30.6 ..	10.2	10.78	
	„ „ „ 28.5 ..	3.2	8.23	0.14
	„ „ „ 25 ..	2.3	6.29	0.02
	„ „ „ 10 ..	5.3	2.74	0.004
	Fraction in solution ..	7.7	0.91	

* Acetone-extracted samples dissolved and dispersed by shaking.

The above data clearly establish that a wide intrinsic viscosity distribution is present in the rubber hydrocarbon in latex, in vacuum dried freshly-coagulated latex and in stored smoked sheet. A considerable volume of data concerning the latter material is already available from the American and European studies[1–7] and the only new aspect of the above data relating to smoked sheet is the relatively small contribution which the gel component makes to the intrinsic viscosity of the total rubber when the latter is dissolved (or dispersed) by shaking. An outstanding feature of all the work in the East, however, is the high order of intrinsic viscosity of a very considerable proportion of the rubber not only in fresh latex but also in the year-old smoked sheet. Few of the American and European studies have revealed fractions with intrinsic viscosities much above 8 in benzene or above 4.5 in benzene + 15% methanol, even when gel has been removed by a preliminary separation, with the exception of some fractions with inherent viscosities up to 14, reported by Johnson[5].

Fractionation of vistex solutions of latex

An alternative approach to the problem of studying the molecular weight distribution in rubber hydrocarbon as it leaves the tree lies in utilisation of the very convenient vistex solution technique referred to in Part I. A mixture of benzene with isopropanol proved eminently suitable for obtaining solutions (which were slightly hazy) of latex from which, by addition of more isopropanol and progressive cooling, a series of fractions including some of a quite remarkable degree of purity were obtained (Table III).

Table III

Fractionation of a vistex solution of latex from tree 3 in benzene-isopropanol.*

Consecutive pptn. temps., °C.	Yield % of rubber	(η)	Analysis		
			N%	Ash %	O%
31.5	23	Insol			
30.5	18	9.7	0.02	0.02	0.09
29.0	15	7.9	0.01	0.04	0.05
10	24	5.8			
Residue ..	20	degraded and contaminated with non-rubbers			

* 10 ml latex in 320 ml benzene + 80 ml isopropanol.

Nitrogenous and insoluble mineral constituents of the non-rubbers were concentrated in the first fraction. These impurities could be reduced by removing the lutoids(8) from the latex by centrifuging for ½ hr. at 2,000 R.P.M. and using the white fraction for preparing the vistex solution (Table IV).

Table IV

Fractionation of a vistex solution of white fraction of tree 14 latex in benzene-isopropanol.

Consecutive pptn. temps.	Yield, % of total rubber	Intrinsic viscosity	Nitrogen content, %
32.5	14.2	Insoluble	2.17
31.3	26.6	11.52	0.33
30.0	15.0	10.48	0.10
28.5	7.4	7.92	0.07
27.0	3.3	6.62	0.03
25.0	2.5	4.14	0.01
10	15.0	2.38	0.003
Residue	16.2	1.29	0.002

The last fractions in the above two fractionations contained the soluble non-rubber substances, and were not examined since they had undoubtedly suffered some degradation during evaporation of the considerable volumes of solution involved. Unfortunately isopropanol has a very great tendency to become peroxidised, which is a factor contributing towards degradation; of alternative solvent pairs benzene-ethanol or benzene-acetone were less effective in concentrating the nitrogenous impurities in the first fraction (Table V).

Table V

Fractionation of a vistex solution of white fraction of tree 14 latex in benzene-acetone.*

Consecutive pptn. temps.	Yield, % of total rubber	Intrinsic viscosity	Nitrogen content, %
29.3°	1.5	—	3.10
28.7°	21.8	Insoluble	1.05
27.5°	28.3	9.10	0.26
26.2°	10.3	6.84	—
25.0°	6.9	6.21	—
22°	1.7	4.42	—
10°	13.2	2.42	—
Residue in solution	16.3†	0.92†	—

* 50 ml. white fraction in 2,000 ml. benzene + 1,300 ml. acetone.

† These figures include the non-rubber substances present.

In order to verify whether there is indeed in fresh rubber a fraction of low intrinsic viscosity or whether those isolated above were cumulative degradation products, some centrifuged white fraction of latex from trees known to give soft rubber was coagulated by pouring into acetone, squeezed into a thin sheet, acetone-extracted at room temperature and dried in vacuo. 50 g. of the dried rubber (intrinsic viscosity 5.7) were dissolved in benzene-methanol, and a major proportion was precipitated by adjusting the methanol concentration to 20% at 30° and then standing in a thermostat at 29°, so yielding 72.2% of precipitated rubber with intrinsic viscosity 6.96 and 23.7%, isolated from solution by evaporation under reduced pressure, with intrinsic viscosity 2.47. The latter material was redissolved in benzene-methanol and again divided into two fractions by adjusting the methanol concentration to 21% and standing at 28.5°, thus precipitating 58.9% with intrinsic viscosity 3.35 and leaving in solution 34.2% with intrinsic viscosity 1.25. The last fraction, a soft, plastic and tacky rubber, represented 8.1% of the original acetone-extracted rubber (Found: C, 85.3; H, 11.8; ash 0.8; O, 1.78)*. Examination of the intrinsic viscosities in relation to the proportions of rubber separated shows that no appreciable degradation can have occurred in these operations.

Osmotic data on pure rubber fractions

The isolation of some pure fractions of reduced molecular weight distribution in the above work has enabled osmotic and viscometric data to be compared.

Osmotic pressure Π (in cm. of benzene) was measured over the concentration range 1 to 8 g. rubber per Kg. solution in the Zimm-Myerson osmometers (see Part I), the dynamic method of Fuoss and Mead[9] being used for solutions which were slow to attain equilibrium. Reduced collodion membranes prepared in England by Dr. F. M. Merrett were sent to Malaya by air in sealed polythene envelopes containing a little water. A set of four osmometers was used in order to avoid having to use the same osmometer for solutions of widely different concentration. Values of Π/C plotted against concentration (g. per Kg. solution) were extrapolated to zero concentration and the molecular weight was obtained from the van't Hoff equation $\Pi/C_0 = 1033 \times .0827\ T/M$ where T is absolute temperature.

* Microanalysis by Dr. W. T. Chambers, (B.R.P.R.A.).

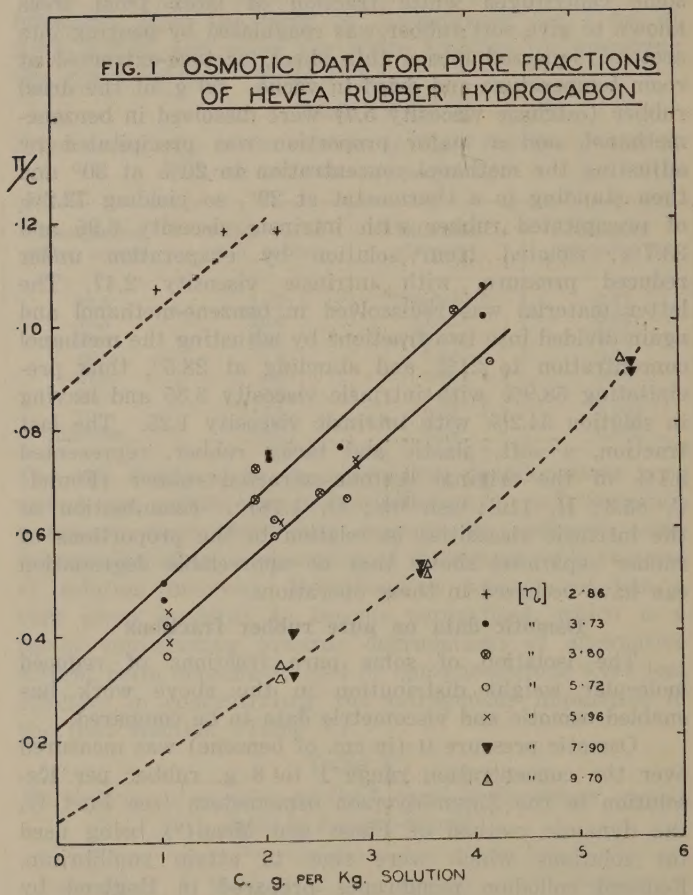
FIG. 1 OSMOTIC DATA FOR PURE FRACTIONS OF HEVEA RUBBER HYDROCABON
π/c
·12
·10
·08
·06
·04
·02
0
1
2
3
4
5
6
C. g. PER Kg. SOLUTION
+ [η] 2·86
• " 3·73
⊗ " 3·80
○ " 5·72
× " 5·96
▼ " 7·90
△ " 9·70

Osmotic data for some of the pure fractions described in the preceding tables are shown in Fig. 1 and the derived molecular weights are shown in Table VI. The spread of the osmotic data is rather greater than is desirable and a very precise extrapolation is not possible; the random error is not yet known. It is however clear that the derived molecular weights are far in excess of those calculated from the linear relationship of intrinsic viscosity used by earlier workers[10,11], and are more nearly representative of those obtained using Magat's numerical values [3] ($K = 5.02 \times 10^{-4}$ and $\alpha = 0.67$ for the constants in Houwink and Flory's equation $[\eta] = KM^{\alpha}$ relating intrinsic viscosity to molecular weight for a variety of linear high polymers[12,13].

Table VI

Intrinsic viscosities and osmotic molecular weights of some hevea hydrocarbon fraction

Intrinsic viscosity	Osmotic M.W.	Viscosity M.W. calculated from $[\eta] = 5.02 \times 10^{-4}\ M^{0.67}$
9.7	$>2.5 \times 10^6$	2.5×10^6
7.9	$>2.5 \times 10^6$	1.8×10^6
5.96 5.72	1.1×10^6	1.2×10^6
3.80 3.73	0.8×10^6	0.6×10^6
2.86	0.25 to 0.35×10^6	0.4×10^6

Huggins[14] has demonstrated from theoretical considerations that the value of the exponent α in the above equation depends on the shape of the polymer molecule. Any factor tending to affect shape, such as chain branching, or tending to restrict free extension of the molecule, such as cross linking, should be effective in reducing the value of the intrinsic viscosity per unit molecular weight which would be reflected in a reduced value of α. This has been verified experimentally for a series of polybutadienes by Johnson and Wolfangel[15], and by Youngson and Melville[16] for branched polyesters. Accordingly, the value 0.67 for α may be too high in the case of the fraction of highest intrinsic viscosity in Table VI since this fraction was observed to give a rather

"ropy" solution in benzene, indicative of incipient gelation. Further measurements proposed in these laboratories will be confined to gel-free material. Similar considerations apply to the discussion in Part II of intrinsic viscosities of sol and gel rubbers, and to the comments on Table II (above).

The influence of polar solvents on intrinsic viscosity

The hypothesis of Alfrey, Bartovics and Mark[17] which explains the behaviour of high polymers in good and in poor solvents in terms of the greater coiling-up of linear molecules in poor solvents, has within recent years been substantiated for several different polymers[18-20]. Kunst[21] measured molecular dimensions in solution by a light scattering method and observed a considerable decrease in size of polystyrene and polyisobutylene molecules on passing from a good solvent to a poor one, especially near the threshold of precipitation. Intrinsic viscosity was dependent on the molecular size rather than on the molecular weight determined osmometrically; polymer homologues of different molecular weight (differing by as much as 3:1) but of the same size in different solvents had nearly the same intrinsic viscosity. The magnitude of this effect may be very considerable when a "good" rubber solvent such as benzene is rendered "poor" by addition of a powerful non-solvent such as methanol to near the critical concentration at which rubber is precipitated from solution. Gee[11] demonstrated that for some crepe rubber examined in England, and for some fractions prepared from it covering the intrinsic viscosity range 1-6 in benzene, the ratio of the intrinsic viscosities in benzene and in benzene + 15% methanol was 1.67. A considerably higher ratio (Table VII) has been observed in the present investigations in Malaya, moreover, the ratio is not independent of intrinsic viscosity but increases with the latter. This behaviour is in accordance with Cragg and Simkins[20] suggestion, derived from theoretical considerations, that the ratio of the length of a fully extended molecule to its length when coiled up should be greater for long molecules and any effect resulting from uncoiling, whether as a consequence of an increase in temperature or of a change from good to poor solvent, should be *relatively* greater for the longer molecules. Cragg and Simkins observed this behaviour with polystyrene fractions.

Table VII

Intrinsic viscosities of rubber in benzene and in benzene + 15% methanol.

Intrinsic viscosities in		Ratio of intrinsic viscosities	Whole rubber (W) or fraction (F)
Benzene	Benzene + 15% methanol		
9.60	3.30	2.9	W
9.11	3.42	2.7	W
8.93	3.33	2.7	W
8.73	3.80	2.3	F
7.74	3.13	2.5	W
7.34	2.98	2.4	W
7.19	3.03	2.4	W
7.12	3.12	2.3	W
5.32	2.39	2.2	Sol rubber
4.64	2.15	2.2	W
2.81	1.57	1.8	F
2.62	1.27	2.1	F
1.05	0.52	2.0	F
0.69	0.36	1.9	F

If the ratio of intrinsic viscosities in good and poor solvents is indeed *consistently* lower in rubber after transportation to Europe or Amercia than in fresh rubber it may indicate that there is considerably more restriction on coiling up in the older samples (e.g. through increased cross-linking), but a complete answer could only be obtained in storage experiments of longer term than has been possible in the present investigations.

It is of interest to compare (unfractionated) rubbers of similar average intrinsic viscosities, but known to be respectively hard and soft, and of high and low gel-content (*cf.* Part II). Table VIII shows that the ratio of the intrinsic viscosities tends to be lower in the high gel hard rubber, consistent with the idea of greater restriction on coiling.

Table VIII

Comparison of intrinsic viscosities of hard and soft rubbers.

Tree No.	Intrinsic viscosity in		Ratio of intrinsic viscosities	Mooney viscosity
	Benzene	Benzene – 10% methanol		
1	5.88	2.22	2.65	47
14	5.88	2.32	2.54	50
15	5.32	2.28	2.33	110
2	5.70	2.43	2.42	110

Restriction on coiling up in poor solvents, arising from branching or cross-linking (probably random cross-linking) is not to be confused with the effect of microgel structure referred to in Part II in which a more localised region of cross-linking, confined to the latex particle, is visualised. Such true microgel can be expected to make relatively little contribution to the overall intrinsic viscosity[22].

The foregoing has some bearing on the relation of elastic properties to intrinsic viscosity, for, as Bardwell and Winkler have pointed out, when cross-linking reactions lead to "clusters" of molecules the observed molecular weight distribution as indicated viscometrically may be severely distorted. Since for satisfactory correlation of elastic properties with molecular weight it is the *primary* rather than the actual molecular weight which should be considered it follows that good correlation of elastic properties with viscosity molecular weight can scarcely be expected[22].

The temperature coefficient of intrinsic viscosity

The rubber molecule in solution cannot be regarded as static. Internal thermal motion results in a continual change of shape as a result of coiling and uncoiling and the most probable average shape will not be the most fully extended one[20]. Hence in a good solvent the intrinsic viscosity may be expected to decrease with any factor, such as a rise of temperature, favouring the more probable configuration whereas in a poor solvent a rise of temperature would increase the asymmetry of the molecule and so *increase* its intrinsic viscosity. These predictions, which have been shown to explain the

behaviour of polystyrene and of GR-S(23) are likewise shown (Table IX) to apply to Hevea rubber by a study of two of the pure fractions (isolated by fractionation of a vistex solution of fresh latex) in a good solvent (benzene) and in a poor solvent (benzene + 15% methanol) over the temperature range 25-35°.

Table IX

The influence of temperature on intrinsic viscosity of rubber hydrocarbon fractions.

Temperature °C	Intrinsic viscosity in		Ratio of intrinsic viscosities
	benzene	benzene + 15% methanol	
25	8.73	3.80	2.3
30	8.46	4.15	2.0
35	8.39	4.24	2.0
25	2.62	1.22	2.15
30	2.59	1.31	2.0
35	2.54	1.45	1.75

Summary and Conclusions

Based on osmotic data the molecular weights of gel-free rubber fractions of narrow molecular weight distribution are not less than those evaluated from intrinsic viscosities by means of the equation $[\eta] = 5.02 \times 10^{4} M^{0.67}$. The use of this equation for a more general interpretation of viscometric data on *unfractionated* rubbers will not however necessarily give results in agreement with osmotic data since the average molecular weight $M_v = \left(\frac{\Sigma N_x M_x^{\alpha+1}}{\Sigma N_x M_x}\right)^{1/\alpha}$ is not identical with the number average (osmotic) molecular weight $M_N = \frac{\Sigma N_x M_x}{\Sigma N_x}$ where M_x is the molecular weight of an x-mer and N_x is the total number of x-mers.

The available osmotic and viscometric data for fractionated rubbers show that normally-tapped Hevea rubber, not only as it leaves the tree, but also in dried freshly-coagulated latex and in year old smoked sheet, comprises a series of polymer homologues in the molecular

weight range 50,000 to over 3 x 10^6. It appears general that a very considerable proportion of the hydrocarbon, at least 60%, has intrinsic viscosity greater than 6, corresponding to molecular weights in excess of 1.3 x 10^6, while a quite substantial proportion is in excess of 2.5 x 10^6. As might be anticipated from Part I there is considerable variation in the proportion of rubber in the high and low molecular weight categories between different trees, and soft rubbers of low average intrinsic viscosity have a higher proportion of components in the low molecular range (below 250,000) than harder rubbers of high average intrinsic viscosity (cf. Table IV of Part I). Generally, the order of magnitude of intrinsic viscosities, and consequently, of the derived molecular weights, is considerably higher than has been observed in European and American studies. No appreciable proportion has been found of any components of molecular weight sufficiently low to classify them as viscous liquids, consequently there is little support for the idea that the softness of the interior of a latex particle([24]), or the capability of latex particles to fuse together([25]), can be attributed to the presence of an elastic outer sheath containing a viscous fluid the proportion of which would be considerable relative to that of the outer shell (cf. also Kemp and Peters([2])).

The interpretation of viscosity data for rubbers containing a considerable gel component is complicated by the fact that the gel component may contribute little to the intrinsic viscosity, especially if it is present as true microgel.

Examination of the effect of addition of non-solvents to rubber solutions in good solvents supports the currently accepted hypothesis that polymer molecules are in general less asymmetric in poor solvents than in good solvents.

Acknowledgments

The authors are grateful to Dr. G. Gee and Dr. F. M. Merrett (B.R.P.R.A.) for helpful advice and criticism. The paper forms part of the programme of fundamental research undertaken by the Boards of the British Rubber Producers' Research Association and Rubber Research Institute of Malaya. The authors particularly desire to record their appreciation of the co-operation of Mr. M. W. Philpott, Head of the Chemical Division of the Rubber Research Institute.

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STUDIES IN HEVEA RUBBER
Part IV
Factors Affecting the Plasticity of Raw Rubber, and Some New Data on Hardening of Rubber by Benzidine

By
George F. Bloomfield

There is no general correlation between intrinsic viscosity and plasticity of rubber apart from a tendency for rubbers of high intrinsic viscosity to be hard and for soft rubbers to have low intrinsic viscosities; the converses are not necessarily true.

Some new data on the hardening of rubber by benzidine show that this does not require the presence of oxygen, although in its absence the hardened rubbers can be brought into solution from treated latices and these solutions show no change in intrinsic viscosity as a result of the hardening reaction.

Acetone-soluble non-rubbers have a considerable influence on the plasticity of raw rubber; acetone-extraction results in considerable hardening without any indication of structural changes in the rubber. Any treatment of latex or rubber which is effective in removing some of these acetone-soluble impurities gives a harder rubber.

It has been established that progressive mill breakdown of a given rubber produces a series of rubbers of progressively reduced intrinsic viscosity and Mooney viscosity in which these two variables are closely related, but it is clear from Tables I, II and III that although there is between *different* rubbers a statistically significant correlation between plasticity and intrinsic viscosity in some cases (e.g. Table III), there are also such wide deviations revealed in the examples shown in Tables I and II that no generalisation can be attempted, and intrinsic viscosity cannot be used as a reliable guide to the plasticity of raw rubber. The sub-divisions of Group G of Table II in particular show that increasing hardness can actually be accompanied by a decrease in intrinsic viscosity.

Table I

Relation between L.S.V. and Mooney viscosity of smoked sheet.

Tree No.	L.S.V.*	Intrinsic viscosity* of pptd. rubber	Mooney* Viscosity
1	4.4	6.9	47
2	4.9	6.5	110
3	4.8	6.6	45
14	5.5	7.6	50
15	5.7	7.3	110
16	6.2	8.5	72
17	7.1	9.0	115

* Means of a year's observations.

Table II

Intrinsic viscosities of latex solutions and of smoked sheet with corresponding Williams plasticities (D_{10} values) and Mooney viscosities.

Source of Latex	L.S.V.	Smoked Sheet		
		$[\eta]$	D_{10} m.m.	Mooney
Group A, 8 trees	5.4	5.53	—	57
„ C, 8 „	5.8	5.61	—	65
„ B, 7 „	6.1	6.12	—	70
„ D, 9 „	6.5	6.18	—	93
„ E, 8 „	7.1	6.73	—	102
„ F, 8 „	7.6	7.25	—	112
„ G, 11 „	6.7	6.35	—	123
„ Ga, 4 „	6.8	—	5.61	120
„ Gb, 3 „	6.5	—	5.58	128
„ Gc, 4 „	6.2	—	5.86	130

(Ga, b, c were sub-divisions of Group G)

Table III

Individual Trees: Intrinsic viscosities of latex solutions, vacuum-dried coagula and smoked sheet, with corresponding Williams plasticities and gel contents.

Tree No.	L.S.V.	Vac-dried coagula			Smoked sheet				Gel in Dried latex
		$[\eta]$	D_{10} m.m.	Rec. m.m.	$[\eta]$	D_{10} m.m.	Rec. m.m.	Gel %*	
1 ..	4.95	4.95	2.89	3.21	4.85	2.89	3.12	51	21
2 ..	5.15	5.66	4.07	5.01	5.59	3.70	4.38	70	59
14 ..	5.25	5.64	3.28	3.67	5.50	3.11	3.35	60	27
19 ..	5.5	6.11	4.33	5.40	5.94	4.07	4.85	77	—
15 ..	5.7	6.66	5.23	7.36	6.16	4.54	5.95	88	71
17 ..	7.6	7.83	5.0	7.6	7.32	5.10	6.94	85	67

* The gel content in this column is defined as that portion of smoked sheet not dissolved on standing with an 80/20 (by volume) mixture of benzene-methanol for 3 days at 30°C., and is not to be confused with the petroleum-insoluble gel described in Part II of this series, and reproduced in the final column of the above Table.

It appears to be generally true that soft rubbers have low intrinsic viscosity, and that rubbers of high intrinsic viscosity are hard, as might be expected in view of the implied differences in molecular weight, and in all probability the range of rubbers examined by van Essen(3) fell into these two categories since his intrinsic viscosities were correlated with Hoekstra plasticities. Some instances occur in the above tables, however, where hard rubbers have only medium or even rather low intrinsic viscosity and these particular rubbers also have high gel contents, determined either on smoked sheet by extraction with 80/20 benzene-methanol or on vacuum dried latex films by extraction with petroleum. Correlation has indeed been found between the Mooney viscosity of smoked sheet and its content of gel insoluble in 80/20 benzene-methanol(2), and it may well be that the plasticity of rubber is very sensitive to the presence of gel whereas the interpretation of viscometric data in terms of molecular weight is greatly complicated by gel. The inverted order of hardness of the rubbers from trees 15 and 17 in relation to their gel-contents however probably reflects the greater average intrinsic viscosity of rubber from the latter tree.

Osmotic molecular weights of hard and soft rubbers of similar intrinsic viscosity

Osmotic data (Fig. I) were obtained for benzene solutions of vacuum-dried coagulated white fractions of the latices of trees 1, 2 and 14. These three rubbers were selected as having very similar intrinsic viscosities but very different plasticities and gel contents. Extrapolation of the osmotic data gave the molecular weights listed in Table IV and these showed considerable differences between the hard and soft rubbers which were not revealed by the intrinsic viscosity measurements. Other differences in the physical state of two of these rubbers, suggesting a greater restriction on uncoiling in the harder rubber, are also shown in Table VIII of Part III.

FIG. 1

OSMOTIC DATA FOR WHITE FRACTION OF RUBBER FROM DIFFERENT TREES GIVING SIMILAR L. S. V.

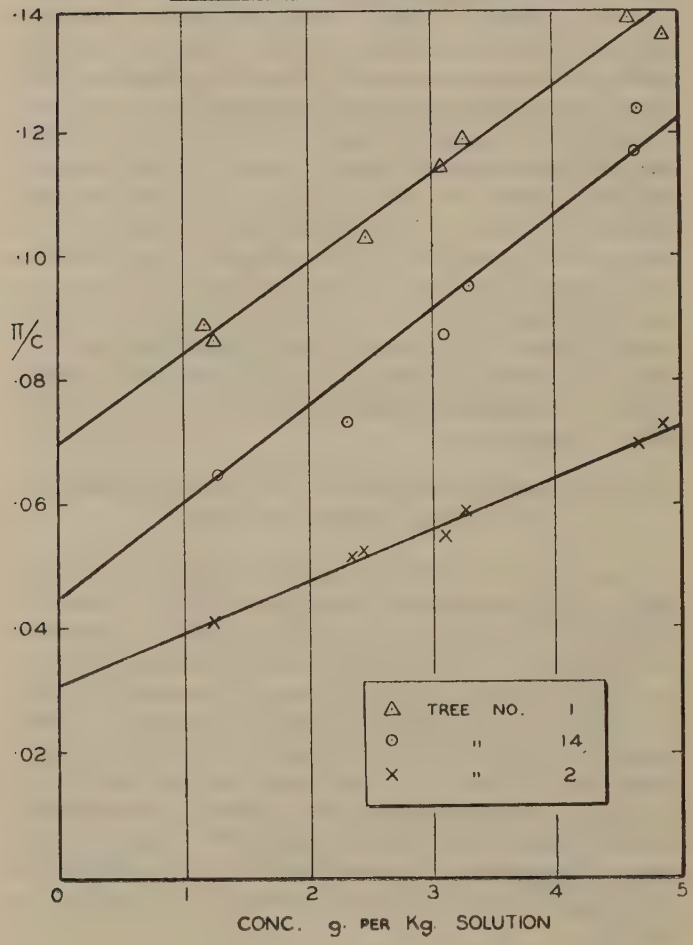

Table IV

Osmotic data on hard and soft rubbers of similar intrinsic viscosity.

Source of rubber	L.S.V.*	Intrinsic viscosity of pptd. rubber*	Osmotic* molecular weight	Mooney† viscosity of smoked sheet
Tree 1	4.9	6.96	367,000	47
„ 14	5.2	7.07	572,000	50
„ 2	5.2	6.60	830,000	110

* Determined on white fraction of centrifuged latex.
† For comparable Williams plasticity data on these rubbers see Table III.

Benzidine-hardening of rubber

A convenient means of hardening rubber artificially is by addition of benzidine hydrochloride to latex prior to coagulation(4) and it is of interest to examine this reaction in relation to changes in intrinsic viscosity and solubility brought about by the benzidine modification. Philpott has presented evidence which suggests that benzidine hardening involves cross-linking by a mechanism not yet established with certainty. If such cross-linking occurs in the latex phase without coalescence of particles it must of necessity be confined to the individual latex particles giving a microgel structure which should be dispersible in solvents on agitation, whereas if cross-linking occurs in the bulk rubber at any stage subsequent to coagulation a macrogel insoluble structure would be expected.

In the above work either benzidine hydrochloride (preferably in suspension) was added to the latex before coagulation, or benzidine was dissolved in the coagulating acid. It is of interest that free benzidine itself is now found to be equally effective when added in aqueous solution to the latex followed by drying the latex in a thin film without acidification (Table V). For comparison the degree of hardening produced by treatment with benzidine hydrochloride is also shown in this table.

Table V

Benzidine hardening of rubber.

Conditions of preparation of samples	Mooney Viscosity	Williams plasticity D_{10} m.m.
(1) Solution of benzidine (0.02 g. in 30 ml. water) added to latex (25 ml.).		
(a) Film dried at 70°C ..	—	6.84
(b) „ „ „ 30°C ..	—	6.37
Control: without benzidine, film dried at 30°C	—	4.50
(2) Conventional acid coagulation and preparation of smoked sheet.		
(a) after adding benzidine (0.1 g.) in water (150 ml). to latex (100 ml.)	151	—
(b) after adding 5 ml. of 2% neutral benzidine hydrochloride solution to 100 ml. latex, followed by 145 ml. water	138	—
(c) control—without benzidine ..	82	—
(3) Conventional acid coagulation and drying of coagula in vacuo.		
(a) as 2 (a) ..	150	7.06
(b) as 2 (b) ..	146½	6.53
(c) control—without benzidine ..	78½	4.30

The effect of benzidine on the solubility of latex and of rubber derived from it is shown in Table VI. Although the latex itself could be brought into solution in benzene as readily as the untreated latex, without significant difference in inherent* viscosity of the resulting solutions, the rubber prepared from this latex, even when dried in vacuo, was difficult to disperse in benzene without violent agitation, while under static conditions it was an insoluble though fairly rigid swollen gel, so resembling a lightly-vulcanised rubber.

* The inherent viscosities of benzidine-hardened rubbers decreased (by about 0.1 units) with a decrease in concentration to 0.6 x c_1.

Table VI

Effect of benzidine on solubility and inherent viscosity.

(40 ml. of 2% neutral benzidine hydrochloride added to 1000 ml. estate latex).

Property measured	Untreated latex (control)	Benzidine-treated latex
Solubility of latex in benzene ..	soluble	soluble
L.S.V. (cf. Part I) ..	5.95	5.91
Inherent viscosity of vacuum dried coagulum	6.54	insoluble*
D_{10} (m.m.) -do- ..	3.88	8.0
D_{10} (m.m.) of smoked sheet	4.07	6.36
Mooney -do- ..	79	135

* This sample was dispersed in benzene after prolonged violent shaking. Its inherent viscosity was then 7.2.

Coagulated benzidine-treated latex rapidly develops a brown discolouration, and in the above experiment it was noticed that the discolouration in the vacuum-dried coagulum was most intense in the surface layer originally uppermost in the coagulating dish, with a gradation of colour through the thickness of the sample. This clear indication that oxidative reactions might have been playing a part in the benzidine hardening led to some trial preparations under conditions rigorously excluding access of oxygen. Tables VII and VIII show that in the absence of oxygen the benzidine-treated rubbers, whether prepared by drying whole latex films or by acid-coagulation and drying, could be brought into solution in benzene with the aid of considerable shaking although the benzene-treated products under static conditions again gave fairly rigid gels. Although soluble, the products were found to be hardened by the benzidine treatment when tested in the Williams plastimeter. From this evidence alone it could not be conclusively argued that the benzidine-treated rubber was in fact already hardened before the plasticity tests were applied since hardening might have taken place at the elevated temperature employed in determining the plasticity. No loss of solubility occurred, however, when a vacuum-dried film prepared from latex containing benzidine was heated for 3 minutes at 100°C in a sealed evacuated tube, and

initially-soluble rubbers containing benzidine were still soluble after testing, hence it seemed unlikely that any structural changes were occurring during the Williams plasticity test; moreover, in the Mooney evaluation benzidine-treated rubbers were invariably extremely hard initially and *softened* during test (cf. Table IX). It therefore appeared certain that the presence of oxygen was not necessary for the fundamental mechanism of hardening by benzidine, although in the presence of oxygen more extensive insolubilisation of the rubber occurred.

Table VII

Properties of vacuum dried film prepared from air-free latex containing benzidine hydrochloride (added as 2% solution to nitrogen-saturated latex)

Properties of dried film	Untreated latex	Benzidine-treated latex
Solubility ..	soluble	soluble
Inherent viscosity ..	6.42	6.45
D_{10} (m.m.) ..	4.30	5.71

Table VIII

Properties of benzidine-treated rubber prepared in absence of oxygen.

Properties of dried sheet	Untreated latex	Benzidine-treated latex, coagulated and dried	
		in air	in absence of air
Colour ..	pale yellow	brown	pale yellow
Solubility ..	soluble	insoluble	soluble on shaking
Inherent viscosity ..	5.96	—	5.99
D_{10} (m.m.) ..	3.75	5.75	5.55

For the coagulation experiments in absence of air, latex was first withdrawn from the tree into a nitrogen atmosphere under sterile conditions, using the apparatus of McMullen[5]. A wide necked bottle was fitted with nitrogen inlet and outlet tubes and a dropping funnel; after displacing the air with nitrogen 20 ml. of the latex were introduced via the dropping funnel, followed by 1 ml. of 2% neutral benzidine hydrochloride solution, 30 ml. of air-free water and 5 ml. of air-free 1% formic acid. Similar quantities of latex were coagulated in air for comparison, one after addition of an equivalent amount of benzidine hydrochloride; coagula were squeezed into thin sheets very rapidly and dried in vacuo at room temperature.

A study of the change in viscosity during test in the Mooney Viscometer, using rubbers prepared as above, showed that the sample prepared under nitrogen was initially the hardest, but gave a slightly lower viscosity after the full three-minute run than the sample prepared in air (Table IX). The addition of sodium bisulphite (0.5% on rubber content of latex) prior to adding the benzidine gave a non-discoloured soluble product without the necessity for excluding oxygen, but although this rubber gave initially high readings it gave a considerably lower viscosity after 3 minutes than the samples without bisulphite, although still harder than the control.

Table IX

Change in viscosity during Mooney evaluation of benzidine-treated rubbers.

Time from start secs.	Untreated latex, coagulated, and vacuum dried	Benzidine treated latex, coagulated and dried		
		in air	in absence of air	in air, after adding bisulphite to latex
11	—	251	—	—
12	—	—	—	220
13	—	—	270	—
14	147	—	—	—
15	142	190	240	216
30	108	170	196	167
45	95	160	172	143
60	87	152	155	124
90	73	147	146	105
120	71½	138	138	96½
150	73	134	127	94
180	74	132	123	95

The data in the foregoing section clearly indicate that plasticity measurements are more sensitive than solution viscosity to the cross-linking attributed to modification of rubber by benzidine.

The effect of purification of rubber on its plasticity

Many instances have been observed where acetone-extraction of rubber in an inert atmosphere, either at room temperature or at the boiling-point of acetone, has markedly increased its hardness. The hardening was accompanied by an increase in viscosity which was not greater than could be accounted for by removal of the 2.5—3.5% of acetone soluble components which are known to reduce solution viscosity (cf. Part I). Coagulation of latex by pouring it into acetone or alcohol similarly led to considerable hardening (Table X).

Table X

Effect of acetone-extraction on intrinsic viscosity and plasticity (Williams, D_{10}) of vacuum-dried coagula.

Treatment	Latex 1			Latex 2		
	$[\eta]$	D_{10} m.m.	Rec. m.m.	$[\eta]$	D_{10} m.m.	Rec. m.m.
Coagulation with formic acid ..	6.75	4.11	5.10	6.39	3.94	5.08
-do- , plus acetone-extraction	7.01	5.05	7.36	6.73	5.13	7.93
Coagulation into acetone ..	7.15	4.13	5.00	6.76	3.92	4.67
-do- , plus acetone-extraction	7.21	5.13	7.50	6.87	5.54	8.99
Coagulation into alcohol ..	—	—	—	6.87	4.57	5.92
-do- , plus acetone-extraction	—	—	—	6.98	5.71	9.19

The degree of hardening appeared at first sight to be rather large in relation to the small amount of acetone-soluble material removed, but the absence of any permanent structural change in the rubber was demonstrated by redissolving the acetone-extract in benzene-alcohol, adding it to a solution of the extracted rubber in benzene, and evaporating the solvents in vacuo, whereby the original plasticity was restored (Table XI). Also of significance was the observation that acetone-extraction did not increase the gel-content of rubber more than could be accounted for by removal of the acetone-soluble components.

Table XI

Effect of restoring the acetone-soluble component of rubber on plasticity of acetone-extracted rubber.

Treatment of rubber (Vacuum-dried coagulum)	D_{10} m.m.	Recovery m.m.
None ..	5.03	7.70
Acetone-extracted ..	5.68	9.52
Restored acetone-extract ..	5.01	6.92

The amount of hardening accompanying purification of the latex itself appeared to depend on the source of the latex (Table XII).

Table XII

Effect of purification and acetone-extraction on plasticity (D_{10} m.m.) of vacuum-dried coagula.

Treatment	Tree 1 Latex		Tree 15 Latex	
Unpurified latex, acid coagulation	2.86	3.07	5.32	8.51
-do- , plus acetone-extraction	3.48	3.99	6.00	10.39
Unpurified latex, coagulated with acetone ..	—	—	5.84	9.15
-do- , plus acetone-extraction	—	—	6.36	11.00
Purified latex*, acid coagulation	3.56	4.69	4.26	6.41
-do- , plus acetone-extraction	4.85	8.91	5.29	9.63
Purified latex, coagulated with acetone ..	—	—	4.86	7.20
-do- , plus acetone-extraction	—	—	6.13	10.85

* Purification by adding ammonium oleate followed by multi-creaming. (The presence of residual soap may have had a softening effect on the unextracted samples).

Summary and Conclusions

Structural changes in rubber attributed to restricted cross-linking have a greater influence on plasticity than on solution viscosity. The interpretation of viscometric data is complicated by the presence of gel in the rubber, consequently there is no general correlation between plasticity and intrinsic viscosity and measurement of the solution viscosity cannot be used as a reliable guide to processing characteristics of the rubber.

The hardening of rubber by addition of a small proportion of benzidine to latex is not dependent on the presence of oxygen, although a rather insoluble and discoloured product is formed when air is not excluded. The inherent viscosity of samples prepared in the absence of air is not significantly affected by the hardening reaction.

Removal of acetone-soluble components of rubber gives a disproportionately large increase in hardness which is not due to any permanent structural change in the rubber.

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